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CADMIUM SOIL SORPTION AT LOW CONCENTRATIONS: I. EFFECT OF TIME, CADMIUM LOAD, pH, AND CALCIUM

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Abstract. Sorption of Cd at low concentrations onto two Danish soils (loamy sand, sandy loam) was examined in terms of kinetics and governing factors. From an environmental point of view soil sorption of Cd is a fast process: More than 95% of the sorption takes place within 10 min, equilibrium is reached in 1 hr, and exposures up to 67 wk did not reveal any long term changes in Cd sorption capacities. The soils have very high affinity for Cd at pH = 6.00 (10^{-3} M CaCl_2) exhibiting distribution coefficients in the order of 200 to 250 (soil Cd concentration/solute Cd concentration). However, the sorption isotherms describing the distribution of Cd between soil and solute are slightly curvilinear. In the pH-interval 4 to 7.7, the sorption capacity of the soil approximately increases 3 times for a pH increase of one unit. Increasing the Ca concentration from 10^{-3} to 10^{-2} M reduces the sorption capacity of the sandy loam to one third.

1. Introduction

The Cd content of Danish soils of agricultural importance is in average $0.22 \mu\text{g}$ ($0.002 \mu\text{mol}$) Cd g^{-1} dry soil (Tjell and Hovmand, 1978) and is estimated to increase $0.6\% \text{ yr}^{-1}$ due to atmospheric deposition and use of phosphate fertilizers (Tjell *et al.*, 1980). Where wastes such as sewage, sewage sludge, and municipal compost are applied to land, the local increase in soil Cd content is much higher. The potential toxicity of Cd to man through contamination of plant produce and drinking water makes knowledge on the soil chemistry of Cd necessary for evaluating the consequences of continued addition of Cd to soils. Several recent studies have examined the soil chemistry of Cd in experiments employing excessive concentrations of Cd (in excess of $20 \mu\text{g}$ ($0.18 \mu\text{mol}$) Cd g^{-1} soil or $100 \mu\text{g}$ ($0.9 \mu\text{mol}$) Cd dm^{-3} solute; Christensen, 1980) and hence with only minor environmental pertinence. Very few studies have been reported on the soil chemistry of Cd at low concentrations (Mayer, 1978; Garcia-Miragaya and Page, 1978; Jarvis and Jones, 1980) revealing mechanisms and parameters relevant for the actual environmental problem of Cd accumulation in soils.

In the present study the sorption of trace amounts of Cd (0.1 to $20 \mu\text{g}$ Cd g^{-1} soil and 2 to $50 \mu\text{g}$ Cd dm^{-3} solute) onto two Danish soils was examined with respect to the effect of time, Cd load, pH, and Ca.

2. Materials and Methods

2.1. SOILS

The soils were sampled in slightly weathered quaternary deposits (tills) formed during the glacial periods (in particular the Weichselian period, approx. 15000 B.C.) from

underlying sediments of different geological age and materials from areas to the north and east of Denmark. The soils consist of a loamy sand and a sandy loam, both sampled in Jutland, Denmark at depths of 50 to 100 cm.

The soils were air dried and sifted through a 0.5 mm nylon mesh. Employing soil fractions less than 0.5 mm instead of less than 2.0 mm improved the precision of batch Cd sorption experiments involving 1 to 2 g of soil from 11.5 to 3.6% (C.V.) (Christensen, 1980). The removed soil fractions (0.5 to 2.0 mm) accounted for 10% of the loamy sand and 25% of the sandy loam.

The soil characteristics, as shown in Table I, were determined primarily by standard methods (Christensen, 1980).

TABLE I
Characteristics of experimental soils

Soil parameters	Loamy sand	Sandy loam
Texture of < 0.5 mm:		
% coarse sand (0.2–0.5 mm)	31.6	16.0
% fine sand (0.02–0.2 mm)	54.7	53.5
% silt (2–20 μ m)	6.8	12.0
% clay (< 2 μ m)	6.2	18.0
% organic matter	0.7	0.5
pH (10^{-2} M CaCl_2)	6.0	6.5
CEC (meq./100 g soil)	7.5	17.6
Metal content:		
Mn ($\mu\text{g Mn g}^{-1}$ soil)		
Dithionite-citrate	82	55
Hot 1:1 HNO_3 for 6 hr	74	110
Fe ($\mu\text{g Fe g}^{-1}$ soil)		
Dithionite-citrate	2790	5560
Hot 1:1 HNO_3 for 6 hr	5800	15100
Zn ($\mu\text{g Zn g}^{-1}$ soil)		
Hot 1:1 HNO_3 for 6 hr	18	29
Cd ($\mu\text{g Cd g}^{-1}$ soil)		
Hot 1:1 HNO_3 for 6 hr	0.03	0.035

Mineral composition of the clay fraction (X-ray analysis of sodium carbonate and dithionite + citrate pretreated clay fractions) of both soils is dominated by the 14-Ångström-minerals (montmorillonite, vermiculite, chlorite). Both contain some hydrous mica, kaolinite, and a little quartz, amphiboles, and feldspar. The loamy sand contains relatively more chlorite and amphiboles, but less hydrous mica and interstratified vermiculite.

2.2. SHORT TERM KINETICS

The rate of Cd sorption onto soil was studied in experiments involving 2 dm³ polyethylene reactors (equipped with stirrer, pH-electrode, and sampling gates), which contained 30 g of soil and 1.5 dm³ 10^{-3} M CaCl_2 solution of preset Cd concentration. At constant pH, samples were taken at varying time intervals, and solute Cd concentrations determined.

2.3. LONG TERM KINETICS

The long term changes in Cd sorption onto soil were studied by means of 0.1 dm³ polyethylene reactors containing 0.5 g of soil per 0.1 dm³ of 10⁻³ M CaCl₂ at preset Cd concentration. The reactors were equilibrated for 20 h at constant pH, and solute Cd concentrations were determined in aliquots of centrifugation supernatants. The reactors were restirred and stored at 1 °C for up to 67 wk. The reactors were briefly shaken once a week. After the extended equilibrium time the reactors were weighed to determine if any losses had occurred, pH was adjusted during a 20 hr period and the solute Cd concentrations determined.

2.4. SORPTION ISOTHERMS

Equilibrium sorption isotherms were determined at different pH-values and Ca concentrations by means of batch experiments involving 0.5 to 4 g of soil in 0.1 dm³ polyethylene reactors containing solutes of preset Cd concentrations. The equilibrations were accomplished at constant pH for 20 hr and the final solute Cd concentration determined.

2.5. GENERAL

Cadmium (based on CdCl₂ standards) was added to the experiments as small volumes of 100 mg (900 µmol) Cd dm⁻³ of 10⁻² M HNO₃. If not stated otherwise, all experiments employed a 10⁻³ M CaCl₂ salt matrix. Based on the stability constants (cited by Hahne and Kroontje, 1973) the Cd chloride complexes should only account for 3% of the Cd in this salt matrix. Other formation constants from the literature indicate a slightly higher degree of Cd-Cl-complex (up to 13% Cd-total), but in the presentation of the results, no distinction between concentrations of Cd-total and Cd²⁺ present in 10⁻³ M CaCl₂ has been made.

All experiments were accomplished at a fixed pH, which was maintained (± 0.03 pH-unit) by addition of HNO₃ or NaOH.

Solute and soil were separated by means of centrifugation corresponding to an equivalent particle diameter of 0.2 µm.

The final soil Cd concentration was routinely calculated from the decrease in solute Cd concentration neglecting the initial soil Cd concentration. This approach was supported by control experiments where measured soil Cd concentrations were only 1.5% less than calculated concentrations (Christensen, 1980).

2.6. CADMIUM ANALYSIS

Solute samples, which were conserved by acidification, were buffered to pH 4 to 6 by addition of trisodium citrate, and Cd extracted by 1% DDDC (diethylammonium-diethyldithio-carbamate) in xylene prior to determination by flameless atomic absorption spectrophotometry (Perkin-Elmer 300 S, HGA 72, deuterium background corrector). The apparatus was adjusted for highest sensitivity (Christensen, 1980). The precision of the Cd determination was estimated to 3% (C.V.).

3. Results and Discussion

3.1. SORPTION KINETICS

The results of the short term kinetic experiments accomplished on both soils are presented in Figure 1 in terms of the solute Cd concentration as a function of the contact time between soil and solute. The results show that more than 95% of the Cd sorption onto soil takes place within 10 min and that a constant distribution of Cd between soil and solute is obtained in 1 hr.

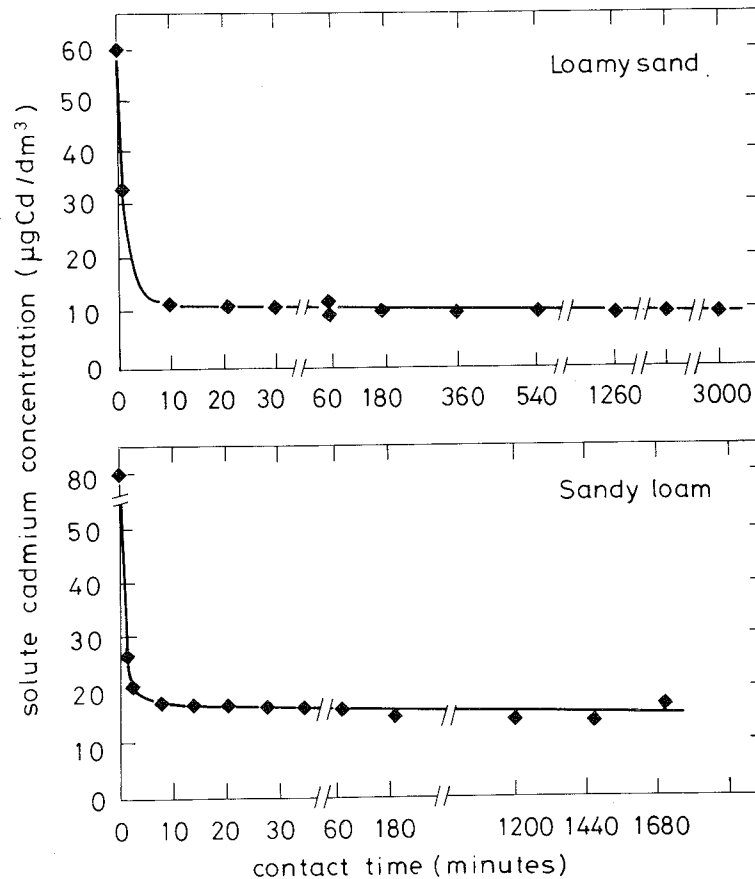


Fig. 1. Solute Cd concentrations as function of contact time between soil and solute.

The results of the long term kinetic experiments involving contact times of 35 and 67 wk are presented in Table II. The ratios between initial (20 hr contact time) and final (35 or 67 wk contact time) solute Cd concentrations are applied for evaluating any long term changes in the distribution of Cd between soil and solute. Calculation of confidence intervals (95%, Student-*t*-distribution) shows a statistically significant 9% decrease in solute Cd concentrations after 35 wk of contact time. However, the experiments running

TABLE II
Data on long term kinetics of Cd sorption (10^{-3} M CaCl_2 ,
pH = 6.00 ± 0.03)

Soil	Solute concentrations, $\mu\text{g Cd dm}^{-3}$			Ratio:* initial divided by final
	initial	final		
	20 hr	35 wk	67 wk	
Loamy sand	18.8	17.5		1.074
	19.5	17.5		1.114
	27.0	26.3		1.027
	20.5	17.5		1.171
	21.3	18.5		1.151
	28.0	25.0		1.120
Sandy loam	18.5	18.3		1.011
	19.5	18.3		1.066
	27.0	26.0		1.038
	28.3	24.8		1.141
	19.0	18.8		1.011
	20.3	19.0		1.068
	19.5	18.0		1.083
	20.0		19.8	1.010
	19.5		21.0	0.929
	17.5		18.3	0.956
	20.0		18.0	1.111
	18.0		18.3	0.984
	19.5		20.0	0.975
	26.8		25.3	1.059
	26.5		26.0	1.019

* Averages and 95% confidence intervals (*t*-distribution) of ratios of initial divided by final concentration are:

a: 1.1087, [1.0535, 1.1639]

b: 1.0617, [1.0189, 1.1045]

c: 1.0064, [0.9578, 1.0550]

67 wk show no changes in solute Cd concentration, indicating that the apparent decrease in solute Cd concentration after 35 wk of contact cannot be interpreted as a slow increase in soil sorption capacity. As presented later, the sorption capacity of soil is extremely sensitive to pH and a pH-bias of the order of 0.1 pH-unit could explain the decreased solute concentration apparently observed after 35 wk of contact.

The kinetic experiments show that from an environmental point of view the soil sorption of Cd is a fast process and that there is no evidence of any significant long term changes in soil sorption capacity due to continued exposure to Cd. Thus equilibrium approaches concerning the soil chemistry of Cd are applicable for evaluation of environmental impacts.

3.2. SORPTION ISOTHERMS

The results of the experiments on Cd sorption from 10^{-3} M CaCl_2 at pH = 6.00 are shown in Figure 2 in terms of isotherms governing the equilibrium distribution between soil and solute. In Figure 3, Langmuir and Freundlich linearizations are shown for sorption data for the sandy loam. Both soils exhibit slightly curvilinear isotherms and very high affinities for sorption of trace amounts of Cd. The distribution coefficient (soil

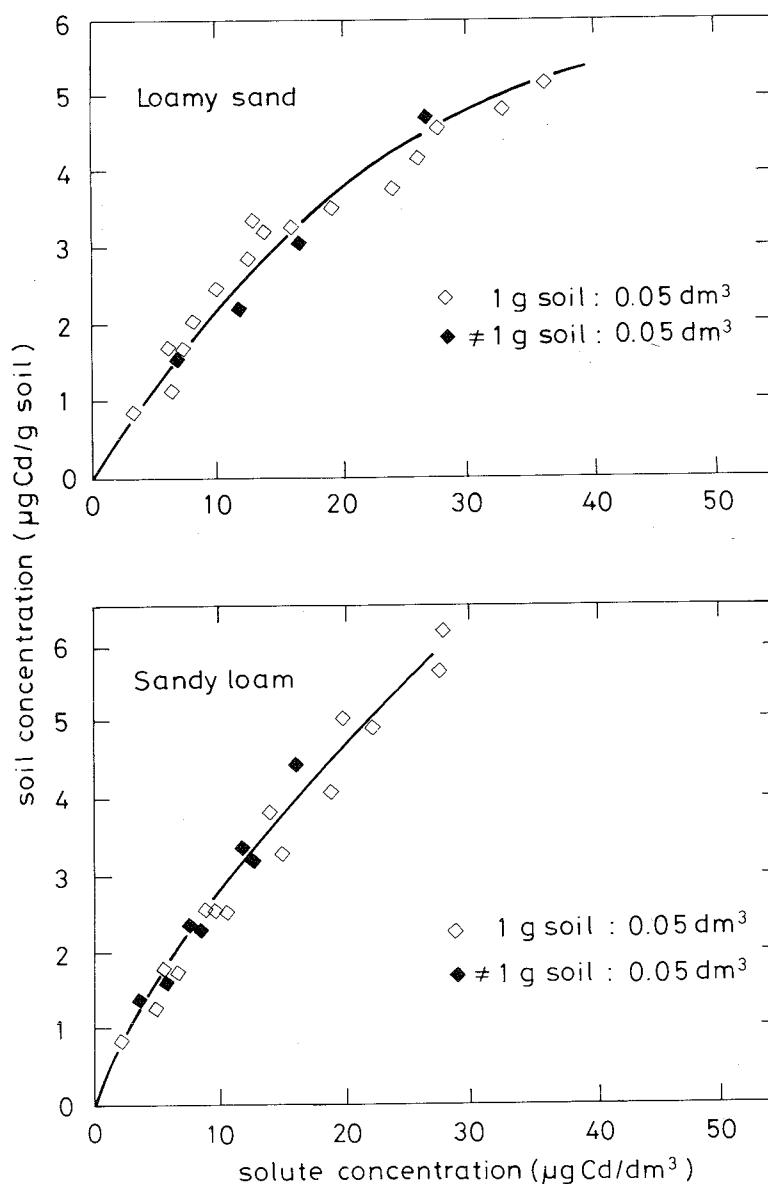


Fig. 2. Sorption isotherms determined in 10^{-3} M CaCl_2 at pH = 6.00.

Cd concentration/solute Cd concentration) at a solute equilibrium concentration of $15 \mu\text{g Cd dm}^{-3}$ is approximately 200 for the loamy sand and 250 for the sandy loam. Such high affinities for sorption of Cd will virtually prevent loss of Cd by leaching from the upper soil layers for decades.

Since the soil Cd concentrations are calculated from the observed decrease in the solute Cd concentration multiplied by the solute to soil ratios, it is important to accomplish the experiments with varying initial solute Cd concentration and at varying solute to soil ratios in order to determine that the results are not affected by the specific experimental set-up. In these experiments the initial solute Cd concentrations varied between 20 and $150 \mu\text{g Cd dm}^{-3}$ and the solute to soil ratios included 0.05 dm^3 to 0.5 to 4 g of soil. It was found that the equilibrium Cd distribution was not affected by the experimental set-up used in this investigation.

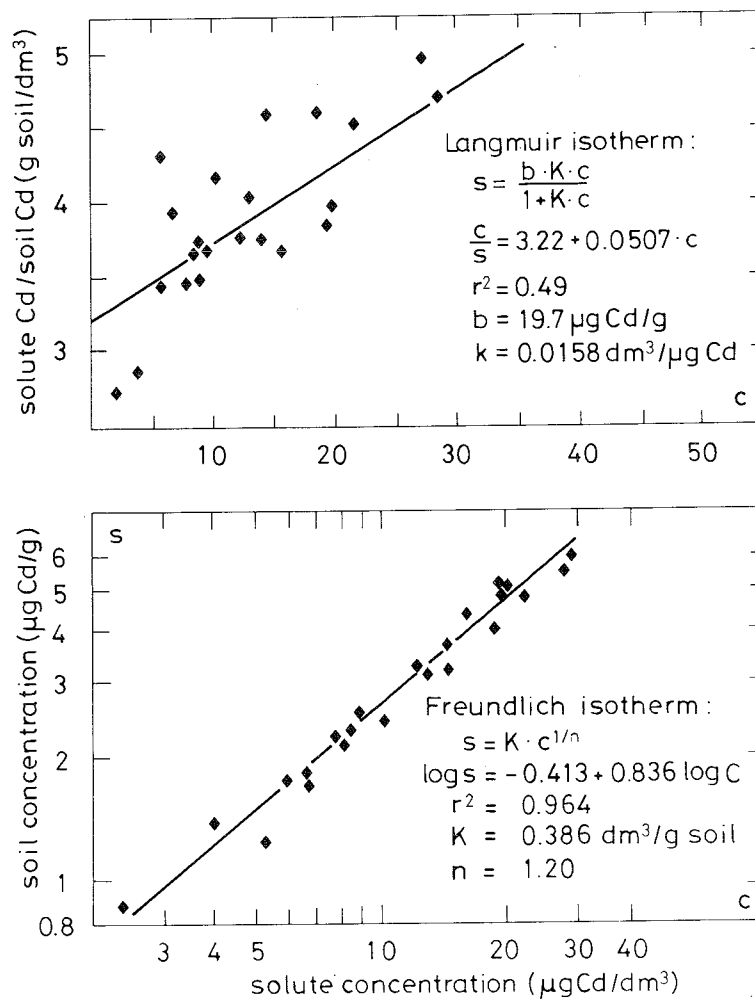


Fig. 3. Langmuir and Freundlich plot of sorption data for sandy loam (10^{-3} M CaCl_2 , $\text{pH} = 6.00$).

Figure 3 shows that for the sandy loam the Freundlich linearization yields a better correlation (r^2) than the Langmuir linearization. However, since the observations fall in the area of an approximate linear distribution of Cd between soil and solute, this fact is not paid much attention, and is not considered to support any hypothesis as to the involved physico-chemical mechanisms. Mathematical equations for the sorption isotherms may on the other hand be valuable approximations describing the distribution of Cd between soil and solute.

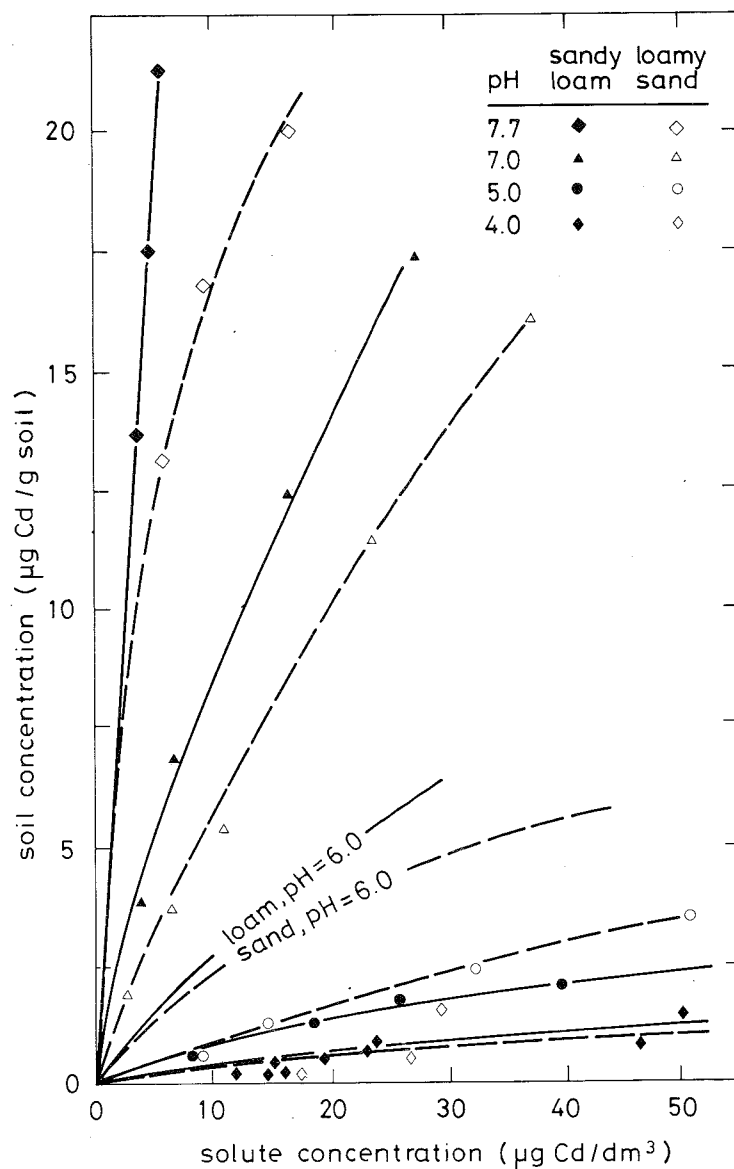


Fig. 4. Sorption isotherms determined in 10^{-3} M CaCl_2 at different pH-values.

3.3. EFFECT OF pH

The sorption isotherms determined for different pH-values (4.0 to 7.7) are presented for both soils in Figure 4. The sorption capacities of the soils are found to increase approximately three times for each increase in pH of one unit in the pH-interval 4 to 7. At low pH-values of 4 to 5, the two soils exhibit about the same capacity to sorb trace amounts of Cd, while the sandy loam has a slightly larger capacity than the loamy sand at higher pH-values (6 to 7). Due to incipient precipitation reactions at pH = 7.7, which presumably could cause coprecipitation of Cd, the sorption capacities of the experimental soils were not examined at pH above this value. These results emphasize pH as the most critical factor in governing the distribution of Cd between soil and solute.

3.4. EFFECT OF Ca

The effects of Ca on the soil sorption of Cd are demonstrated in Figure 5, where the Cd sorption isotherm for the sandy loam at pH = 6.00 determined in 10^{-2} M CaCl_2 is compared with that valid for sorption in 10^{-3} M CaCl_2 . Changing the salt matrix from 10^{-3} to 10^{-2} M CaCl_2 results in a 5 to 6 times decrease in soil sorption capacity for Cd. This effect, however, is a combination of reduced activities (due to increased ionic strength and chloride complex formation) and competition by Ca for soil sorption sites. The effects of the Ca competition alone can be observed if the results are 'normalized' with respect to the activity of the free metal, Cd^{2+} . The activity of Cd^{2+} is calculated (based on stability constants cited by Hahne and Kroontje, 1973) as 0.761 times the total Cd concentration in a 10^{-3} M CaCl_2 salt matrix and 0.424 times the total Cd concentration in a 10^{-2} M CaCl_2 salt matrix accounting for complex formation and ionic strength (Christensen, 1980). Multiplying the total Cd concentration observed in the 10^{-2} M CaCl_2 by the ratio $0.424/0.761$, makes these observations, with respect to activities, comparable to the total concentration measured in 10^{-3} M CaCl_2 . The results of this transformation are also shown in Figure 5. The difference between the

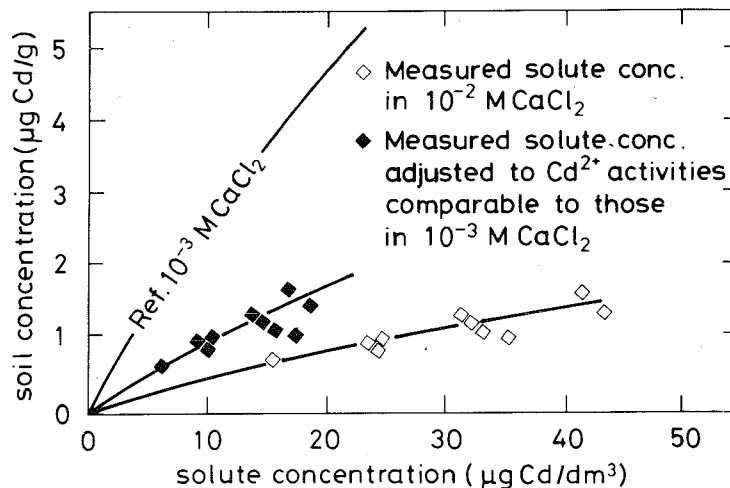


Fig. 5. Sorption isotherms for sandy loam determined in 10^{-2} M CaCl_2 at pH = 6.00.

10^{-3} M CaCl_2 isotherm and the transferred isotherm expresses the reduction in soil sorption capacity for Cd caused by Ca competition. An increase in Ca concentration from 10^{-3} to 10^{-2} M is found to reduce the Cd sorption capacity of the sandy loam approximately to one third. This fact may significantly affect the distribution of Cd between soil and solute, and hence the availability of Cd to plant uptake and leaching, since it is common that Ca concentrations of soil solutions vary widely as a function of time.

4. Conclusion

Based on experiments with two soils exposed to low concentrations of Cd, it is concluded that:

- From an environmental point of view soil sorption of Cd is a fast process (more than 95% sorption within 10 min) and no long term changes in Cd distribution has been found.
- Cd soil sorption isotherms are slightly curvilinear approaching linear distribution coefficients of the order of 200 to 250 for the experimental soils at pH 6.00.
- pH is an extremely important factor in controlling Cd distribution in soils. In the pH interval 4 to 7.7 the sorption capacity of the soils increased 2 to 3 times for a pH increase of one unit.
- Ca present in the soil solution is found to compete effectively with Cd for sorption sites in the soil.

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